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SYNTHESIS OF COMPLEX OXIDES OF RARE ELEMENTS OF GROUPS IV AND V (A REVIEW)

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The prospects of using various methods of synthesis for producing extra-pure complex oxides of alkali and bi-valent elements with rare elements of groups IV and V of precisely prescribed chemical and granulometric compositions are analyzed. It is demonstrated that only the sol-gel method with inorganic precursors yields nanosize powders of narrow granulometric classes. Epitaxial coatings based on complex oxides can be synthesized by the sol-gel method using organic precursors or true solutions of reactant components.

Tantalates and niobates of alkali elements, titanates and zirconates of magnesium, strontium, barium, and lead, as well as solid solutions based on them possess ferroelectric and nonlinear-optical properties and can be used in the form of monocrystals, ceramics, micro- and nanosize powders, or thin films. The purpose of our study is the comparative evaluation of methods for synthesizing such compounds.

The most common is the sintering method when initial components are mixed, the mixture is charged into cuvettes and subjected to heat treatment. Depending on the composition of the product synthesized and the choice of initial components, heat treatment is performed at a temperature of 900–1300°C. The process depends on the diffusion of the low-melting component into the grains of the component with the higher-melting temperature. At early stages, compounds with the maximum absolute variation in Gibbs' energy are formed [1]. They have a higher melting or decomposition temperature than other compounds present in the system. If an intermediate phase emerges in synthesis, whose melting temperature is higher than the melting temperature of the initial components, it acts as a barrier determining the process kinetics.

As a rule, a series of intermediate compounds are formed. For instance, in the synthesis of $\text{Pb}(\text{NbO}_3)_2$ by sintering Nb_2O_5 and PbO [2], initially a multiphase layer is formed on the surface of Nb_2O_5 particles, which contains $3\text{PbO} \cdot \text{Nb}_2\text{O}_5$, the solid solution $5\text{PbO} \cdot 2\text{Nb}_2\text{O}_5 - 2\text{PbO} \cdot \text{Nb}_2\text{O}_5$, and $3\text{PbO} \cdot 2\text{Nb}_2\text{O}_5$; in doing so, PbO is fully consumed. The phases $\text{PbO} \cdot \text{Nb}_2\text{O}_5$ and $\text{PbO} \cdot 2\text{Nb}_2\text{O}_5$ have not been registered in the reaction product layer, which contradicts the common assumption that all phase existent in a system should be formed sequentially. At the second stage,

$3\text{PbO} \cdot \text{Nb}_2\text{O}_5$ is consumed and the layer of the solid solution $5\text{PbO} \cdot 2\text{Nb}_2\text{O}_5 - 2\text{PbO} \cdot \text{Nb}_2\text{O}_5$ increases significantly. At the third stage, PbO is removed from the solid solution, reaching the ultimate composition of $2\text{PbO} \cdot \text{Nb}_2\text{O}_5$. Next, a lead metaniobate layer emerges and slowly grows, whereas the thickness of the layer $3\text{PbO} \cdot 2\text{Nb}_2\text{O}_5$ increases sharply due to the transformation of $2\text{PbO} \cdot \text{Nb}_2\text{O}_5$ into the specified phase. When $2\text{PbO} \cdot \text{Nb}_2\text{O}_5$ nearly disappears, the lead metaniobate layer is just a few nanometers thick and the reaction product is mainly represented by the phase $3\text{PbO} \cdot 2\text{Nb}_2\text{O}_5$. Finally, the layer $\text{Pb}(\text{NbO}_3)_2$ formed in the reaction of $3\text{PbO} \cdot 2\text{Nb}_2\text{O}_5$ with Nb_2O_5 becomes expanded.

The efficiency of synthesis increases as the grain size of initial reactant powders decreases. To obtain a more homogeneous products, it has been proposed to conduct sintering in two stages with additional milling and mixing of partly reacted mixture. However, even multiple heat treatment did not ensure the synthesis of homogeneous products, for instance, solid solutions $\text{K}(\text{Ta}_{0.5}\text{Nb}_{0.5})\text{O}_3$ [3].

The sintering method does not ensure products with a precisely specified ratio of oxides due to the significant error in determining the content of the main compound of the reactant components and also due to the formation of byproduct microimpurities.

The local concentration gradients that determine the rate of diffusion decrease during the process. This is the reason for the need for protracted high-temperature treatment of mixtures and increased electricity consumption, as well as the reason for the formation of phases whose oxide ratio differs from the required composition. Such phases also arise as a result of insufficient quality of mixing initial components and different diffusion coefficients of the reactant cations, due to which the surface of the synthesized material grains has a perceptible concentration of the component with the

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higher diffusion coefficient. Thus, the surface of SrTiO_3 grains becomes rich in SrO and the surface of BaTiO_3 rich in BaO , which in air transforms into BaCO_3 [4]. However, if the synthesized product is used for growing single crystals, its composition is homogenized in melting. The process becomes much more complicated if one of the components can volatilize in heating or if there exists an intermediate high-melting compound on the phase diagram between the lower-melting initial compound and the target product. In order to preserve high purity of products, one needs expensive equipment. It is difficult to ensure the required sterility in mixing, briquetting, and sintering. Finely disperse powders cannot be produced by the sintering method.

To accelerate the process of producing complex oxides and improve their quality, it is proposed to use self-propagating high-temperature synthesis. Titanates and zirconates of alkaline-earth metals have been produced by reactions between $\text{M}(\text{NO}_3)_2$, $\text{TiO}_2(\text{ZrO}_2)$, and C [4]. Although the duration of synthesis and electric consumption decrease with this method, the majority of the technological problems inherent in sintering persist.

The rate of synthesis increases notably and the process temperature decreases when solid-phase synthesis is performed in the presence of a liquid phase [1]. The liquid phase is formed either due to using a low-melting component, usually nitrate of alkali or alkaline-earth elements, due to the introduction of additives forming relatively low-melting eutectics, or due to conducting synthesis in salt melts that do not form compounds with the initial and final products [5–7]. However, the use of nitrates leads to the emission of nitric oxides, and when fluxes or a salt bath are used, the additionally used reactants have to be separated, which is virtually impossible to attain.

The homogeneity of mixing is improved by mechanochemical treatment, providing a tight contact and renewal of the surface and the formation of a highly defective structure, which accelerates mass transfer processes. Reactions in mixtures of hydrated oxides are thermodynamically more efficient than in mixtures of anhydrous oxides. The completeness of the reaction depends on the duration of mechanochemical treatment, the electric intensity of the equipment, and the chemical activity of the batch components; however, the reactions of synthesis are not completed and a subsequent high-temperature treatment of the mixture is required [8].

Mechanochemical synthesis decreases the temperature and duration required for finish heat treatment; however, energy consumption remains high, since mechanical activation is very energy-consuming. This method does not ensure a product with a precisely specified composition; furthermore, the degree of contamination of the synthesized product grows due to the abrasive wear of the equipment. Although this synthesis produces nanosize grains and the finish heat-treatment temperature decreases, such grains in sintering form agglomerates of several micrometers. As a consequence, the method does not ensure the production of nanosize powders of narrow size classes.

Homogeneous precursors can be synthesized using true solutions of reactant compounds. It has been proposed to process them either by plasma chemical treatment, or by the coprecipitation of components or their compounds and then heat-treating the precipitate. Powders of lead zirconate-titanate were obtained by plasma chemical treatment of solutions containing nitrates of metals [9]. The product contained not more than 60% lead zirconate-titanate, oxides, and nitrates and required additional heat treatment at 1150°C .

Chelate solutions can be used, but this method is not promising due to its complicated technology, a relatively high cost of reactants, and the absence of any additional advantages [10]. It is possible to synthesize MgTiO_3 by coprecipitation of magnesium and titanium from their mixed sulfate solution using NaOH [11]. The drawbacks of this method include the difficulty of removing the sulfate ion and the impossibility of using this method for synthesizing strontium, barium, or lead titanates.

To synthesize CaTiO_3 , titanium hydroxide was dissolved in a mixture of ammonia and hydrogen peroxide [12]. After $\text{Ca}(\text{NO}_3)_2$ solution was added, a precipitate was formed in which $\text{Ti} : \text{Ca} : \text{O}_{\text{act}} : \text{H}_2\text{O} = 1 : 1 : 3 : 3$. Within 24 h a steady complex with $\text{Ti} : \text{O}_{\text{act}} = 1 : 2$ was produced. The splitting off of oxy groups and water was observed at $98 - 170^\circ\text{C}$ and the crystallization of CaTiO_3 was registered at 600°C .

BaTiO_3 , $(\text{Ba}, \text{Sr})\text{TiO}_3$, and PbTiO_3 were obtained from previously precipitated binary oxalates of a bivalent metal and titanium (RF patent No. 2060946). The initial compounds included titanium oxychloride, titanium chloride, or titanium oxalate, zirconium and barium chlorides, and lead oxalate; in some occasions hydrogen peroxide was added to keep the titanium in solution. The study of the thermal decomposition of $\text{BaTiO}(\text{C}_2\text{O}_4)_2 \cdot 4\text{H}_2\text{O}$ indicates that it proceeds in four stages, i.e., dehydration, decomposition, crystallization, and formation of BaTiO_3 [13]. A certain amount of TiO_2 and BaCO_3 was formed during decomposition in air. The major part of the intermediate phase had the composition of $\text{Ba}_2\text{Ti}_2\text{O}_5\text{CO}_3$. The entire BaTiO_3 was obtained in a nitrogen medium as a result of decomposition of the intermediate phase, whereas in air a part of the BaTiO_3 was formed through the reaction between BaCO_3 and TiO_2 .

Compared to the sintering method, the oxalate method provides a substantial decrease in the temperature of synthesis ($600 - 700^\circ\text{C}$) and the duration of calcination (2 h) and, accordingly, decreases energy consumption [14]. The resulting powder has grain size of $0.2 - 2.0 \mu\text{m}$. The use of this BaTiO_3 powder significantly improves the quality of ceramics [14]. However, the atomic ratio of $\text{Ba} : \text{Ti}$ in the synthesized BaTiO_3 is equal to $0.98 - 1.02$ and the residual weight content of carbon in the surface layer of ceramics is 0.04% [15]. Consequently, this method does not guarantee the synthesis of strictly stoichiometric products in the form of nanosize powders with a narrow granulometric composition.

Peroxide precursors have been used to synthesize LiNbO_3 , LiTaO_3 , and solid solutions $\text{Li}_x\text{Na}_{1-x}\text{NbO}_3$ [16].

Hydroxides taken in a stoichiometric ratio were dissolved in hydrogen peroxide. After the solutions were heated and boiled down, precipitates were formed. The compositions of the settling complexes remained unchanged during their precipitation. For instance the empirical formula of the precipitate in the synthesis of LiNbO_3 corresponded to $\text{Li}_2\text{O} \cdot \text{Nb}_2\text{O}_5 \cdot 3\text{H}_2\text{O}_2 \cdot 3\text{H}_2\text{O}$. After the precipitate was rinsed with ethyl alcohol, it transformed into $\text{Li}_2\text{O} \cdot \text{Nb}_2\text{O}_5 \cdot 2\text{H}_2\text{O}_2 \cdot 1.5\text{H}_2\text{O}$. Heating these precipitates to $650 - 730^\circ\text{C}$ yielded crystalline target products. A decreased content of chemically fixed hydrogen peroxide and water resulted in a perceptible decrease in the size of particles (grains and grain conglomerates) of lithium metaniobate.

The use of true solutions of reactant components makes it possible to have more homogeneous compositions in the products, to achieve heat treatment temperatures that are lower than those used in the sintering method, and sometimes to obtain additional purification of precursors during their chemical precipitation. Some techniques are promising for producing epitaxial films of nano- and microsize thickness [17].

The methods of sol-gel synthesis of complex oxides using organic (usually alcoholate) or inorganic compounds of metals have been intensively researched. The alkoxide technology is used to produce and hydrolyze alcoholate solution in an organic solvent. The hydrolysis of such solution produces insoluble bimetallic oxyalcoholates, which ensures the homogeneity of future complex oxides at the atomic level. The oxyalcoholates are separated and dried. The final synthesis is performed by calcination at a temperature lower than that used in synthesizing similar materials by the sintering method [18]. The powders of alkaline-earth titanates produced using this technology consisted of crystallites not larger than $1\text{ }\mu\text{m}$. Their application decreases the sintering temperature by at least 200°C [18]. The powders of LiNbO_3 produced by calcination at a temperature of $350 - 400^\circ\text{C}$ had a particle size of $0.2 - 5.0\text{ }\mu\text{m}$ (USSR Inventor's Certif. No. 1101413). Alkoxide solutions can be used in the production of epitaxial coatings [19].

The possibility of partial replacement of alkoxides by inorganic compounds has been demonstrated. For instance, in the synthesis of LiNbO_3 and LiTaO_3 it is possible to use solutions of inorganic lithium compounds in ethyl or methyl alcohol (U.S. patent No. 4108970) instead of lithium alkoxides.

Thus, the alkoxide method makes it possible to synthesize rather high-quality products and is suitable for producing epitaxial coatings. However, alkoxide compounds are expensive fire-hazardous, and involve complicated techniques.

When alkoxides are produced by anode dissolution of metals in absolute alcohols in the presence of a conducting additive, for instance, lithium chloride (RF patent No. 2049065), the latter contaminates the synthesized product. The errors made in determining the concentration of components in the initial alkoxide solutions and the use of

conducting additives for their synthesis are responsible for deviations from a prescribed composition. This method does yield nanosize powders of narrow granulometric classes. To prevent the formation of intermediate carbonate phases due to the sorption of carbon dioxide from the air atmosphere, it is recommended to perform hydrolysis in a nitrogen atmosphere and to dry the hydrolyzed product in vacuum [20]. To prevent the contamination of the product with carbon, it is advisable to conduct calcination in a N_2O atmosphere, since the oxidizing effect of oxygen was found to be insufficiently effective [21].

The inorganic precursors used for elements of groups IV and V are gel-like oxyhydroxide compounds of titanium, zirconium, niobium, and tantalum produced, as a rule, by aqueous hydrolysis from chlorides (USSR Inventor's Certif. No. 570553). The chlorides are hydrolyzed from aqueous solutions of ammonia, as well as lithium hydroxide and carbonate [22].

Two mechanisms have been proposed for the formation of BaTiO_3 when titanium hydroxide gels are treated with barium compounds in an aqueous medium [23 – 25]:

- the cation Ba^{2+} diffuses via the BaTiO_3 layer formed on the surface of a titanium hydroxide particle and then reacts with the nucleus of the titanium hydroxide particle; the rate is controlled by the diffusion rate or the chemical reaction rate; BaTiO_3 particles produced according to this mechanism should preserve the size and morphology of their precursors, i.e., titanium hydroxide particles;
- titanium hydroxide becomes dissolved and reacts with complexes containing barium cations; the resulting BaTiO_3 precipitates from the solution; if this mechanism is true, BaTiO_3 particles should differ in size.

Under a stoichiometric consumption of the reactants, the atomic ratio of $\text{Ba} : \text{Ti}$ in the synthesized crystals was equal to 0.635 ± 0.005 . The atomic ratio of alkali or bivalent elements to the elements of groups IV and V required for complete synthesis significantly exceeded unity, which points to process according to the first mechanism prevailing [24]. This, as a rule, is responsible for an enhanced concentration of alkali or bivalent elements in synthesized complex oxides. If the intermediate oxyhydroxide precursor after its separation from the mother solution requires additional high-temperature treatment, it should be performed at a temperature excluding the occurrence of secondary reactions of the precursor with excessive alkali or bivalent element compounds. After the end of synthesis, the excessive amount of these compounds was removed by rinsing in water and in the case of BaTiO_3 — with low-concentration formic acid.

However, it is difficult to obtain products of a strictly stoichiometric composition using this method. Thus, for 30% excess the ratio $\text{Li} : \text{Nb}$ in LiNbO_3 was equal to 1.003 ± 0.005 , and for 10% it was only 0.996 ± 0.005 (USSR Inventor's Certif. No. 570553).

Depending on the process conditions, powder with grain size ranging from a few tens to a few hundred nanometers

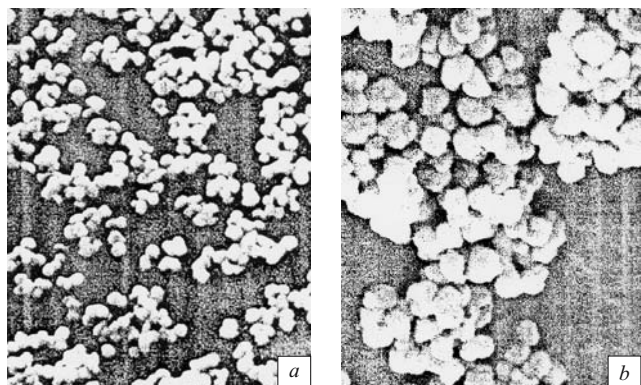
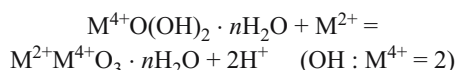


Fig. 1. Microphotos of powders SrTiO_3 , BaTiO_3 , and PbTiO_3 obtained upon the formation of particles in an aqueous suspension for 40 min (a) and 120 min (b).

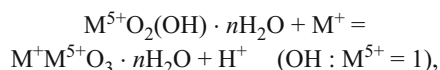
have been produced. Freezing titanium oxyhydroxide gel before synthesis yields BaTiO_3 powders with a grain size of $0.05 - 0.10 \mu\text{m}$ [26].

A method has been developed for producing pure monodisperse nanocrystalline microspheric powders BaTiO_3 and SrTiO_3 , according to which first monosize ($0.1 - 1.0 \mu\text{m}$) particles of titanium or zirconium hydroxide are synthesized by hydrolysis of TiCl_4 or ZrOCl_2 in mixed water-alcohol solutions (U.S. patent No. 6264912). The size and morphology of titanium or hydroxide particles are controlled by varying the concentration of isopropanol and, accordingly, the dielectric permeability of the solutions. At the second stage, composite oxides materials were obtained by a low-temperature (not more than 100°C) hydrothermal reaction of titanium or zirconium hydroxide with barium or strontium compounds. It is reported that the size and morphology of BaTiO_3 particles remained the same as in the microspheres of the titanium hydroxide precursor, which points to the mechanism involving the diffusion of Ba^{2+} via the BaTiO_3 layer formed on the titanium hydroxide particle. Barium carbonated was removed from resulting BaTiO_3 by rinsing with formic acid.

The methods of sol-gel synthesis of complex oxides are based on the concept that the hydrolysis of salts of group IV and V elements produces oxyhydroxides with the respective empirical formulas of $\text{M}^{4+}\text{O}(\text{OH})_2 \cdot n\text{H}_2\text{O}$ and $\text{M}^{5+}\text{O}_2(\text{OH}) \cdot n\text{H}_2\text{O}$. In synthesis the oxyhydroxides react with the cation of the alkali or bivalent metal according to the following reactions:



or



forming hydrated complexes that, as a rule, are amorphous. Since oxyhydroxides are amorphous and contain plenty of water, the cation exchange reactions should be rather fast.

Subsequent heat treatment leads to the formation of dehydrated products and their crystallization.

However, during the hydrolysis of salts and subsequent olation-oxolation reaction typical of oxyhydroxides of group IV and V elements the molar ratios $\text{OH} : \text{M}$ may vary within a perceptible interval [27]. Therefore, the number of hydroxyl group protons replaced by the cations of alkali and bivalent elements is not constant, which may disturb the stoichiometry of compounds. Identifying the conditions for the production of precursors with the required ratio of cation-exchange groups to the atoms of group IV or V elements would improve the efficiency of synthesis of complex oxides using this method.

We have established that as the duration of mixing nanosize powders SrTiO_3 , BaTiO_3 , and PbTiO_3 synthesized in aqueous media increases, the size of the powder particles grows (Fig. 1). The variation in the particle size does not depend on a particular bivalent element. The obtained data cannot be attributed to the dissolution and recrystallization of the synthesized products, since in such a case the products should contain finer particles as well. It can be assumed that nanosize powders obtained in sol-gel synthesis consist of conglomerates of significantly finer crystalline grains. A part of these conglomerates disintegrate in mixing because of collisions, but the emerging "fragments" quickly become captured by surviving stronger particles.

The sol-gel methods make it possible to raise the quality of complex oxide, to produce them in the form of finely dispersed powders of narrow granulometric classes, and to use intermediate gels for producing epitaxial films.

To conclude, note that methods for estimating component ratios in synthesized products should be refined, since the proposed chemical methods are not sufficiently accurate [28] and the physical methods are not applicable to analyzing compositions of complex oxide powders; however, they can be used to indirectly infer the ratio of components in monocrystals or ceramics produced from complex oxides.

Thus, the sintering method is suitable for high-output machinery; however, is energy-consuming and does not produce homogeneous products of precisely prescribed composition in the form of finely dispersed powders. The use of self-propagating synthesis shortens the duration and decreases energy conduction but does not eliminate the majority of the drawbacks inherent in the sintering method.

Mechanochemical synthesis improves the homogeneity of the product; moreover, the duration and temperature of synthesis decrease perceptibly and energy consumption decreases to a lesser extent; however, we do not get products of precisely prescribed composition, and the contamination of the product increases due to abrasive wear of the equipment used for mechanochemical activation. After mechanical activation, additional high-temperature treatment is required to complete synthesis. This method does not yield nanosize powders of narrow grain size classes.

The use of true solutions of precursors and subsequent plasmachemical treatment or calcination of precipitates formed in the coprecipitation of precursor compounds generally makes it possible to synthesize much more homogeneous products. However, considering the complexity of particular technological solutions, the relatively high cost of reactants, and the absence of other advantages in most cases, this method is only promising for obtaining products in the form of epitaxial coatings on substrates. Nanosize powders of complex oxides cannot be produced using this method.

The methods of sol-gel synthesis of complex oxides using organic precursors decrease energy consumption and yield more disperse powders than the sintering method (although the powders are not nanosize of narrow size classes). However, it is difficult to synthesize products of a strictly preset composition and to fully remove carbon and its derivatives. Alkoxide components are expensive and inflammable, and their application requires complicated equipment.

The methods of sol-gel synthesis of complex oxides using inorganic precursors are free from many drawbacks arising in using organic precursors. In some cases they allow for the synthesis of target products directly in the pulp, not requiring further high-temperature treatment, which allows for producing narrow granulometric classes of nanosize powders with a preset characteristic average size. It is difficult to get strictly stoichiometric compositions using these methods.

Epitaxial coatings based on complex oxides can be synthesized by the sol-gel method using organic precursors or true solutions of reactant components.

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